



# Multiscale Modeling of UHTC: Thermal Conductivity

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*NASA Innovative Partners Program (IPP)*



# Materials Modeling at NASA ARC

## **New materials modeling: interdisciplinary**

- Computational chemistry
- Computational physics
- Computational engineering

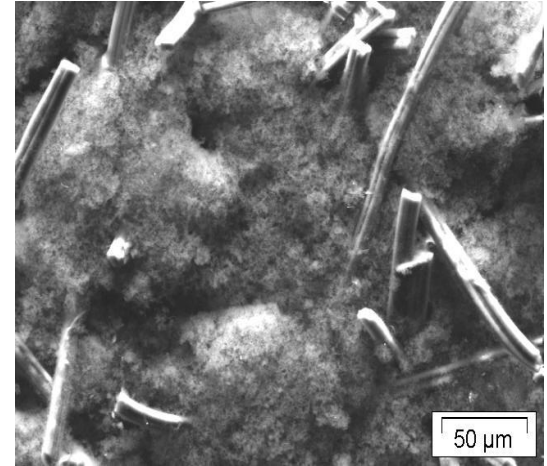
## **Ablative composites**

- Application: atmospheric re-entries
- Materials: PICA, Avcoat,...

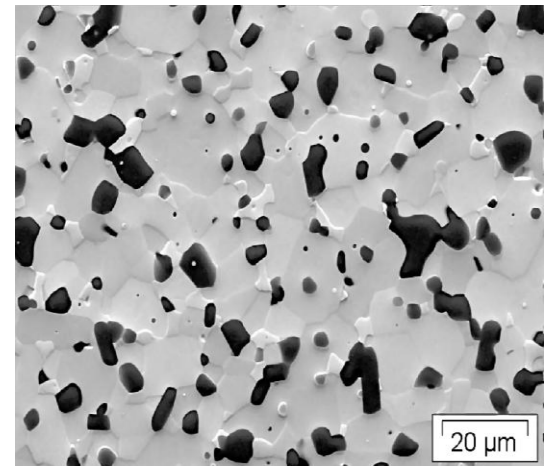
## **Ultra high temperature ceramics (UHTC)**

- Applications: leading edges
- Materials:  $\text{ZrB}_2$  and  $\text{HfB}_2$

## **UHTC modeling illustrate our approach**



*PICA: fibers w/ phenolic*



*UHTC:  $\text{HfB}_2$  w/ 20% SiC*



# UHTC for Sharp Leading Edges

## ***Sharp leading edge for hypersonic aircraft***

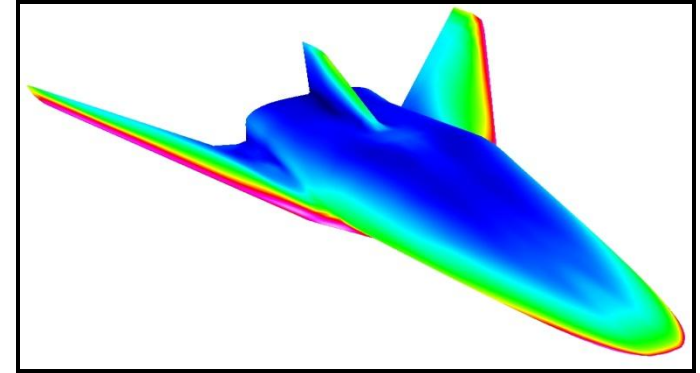
- Enhances vehicle performance
- Improves safety

## ***Higher temperature requirements***

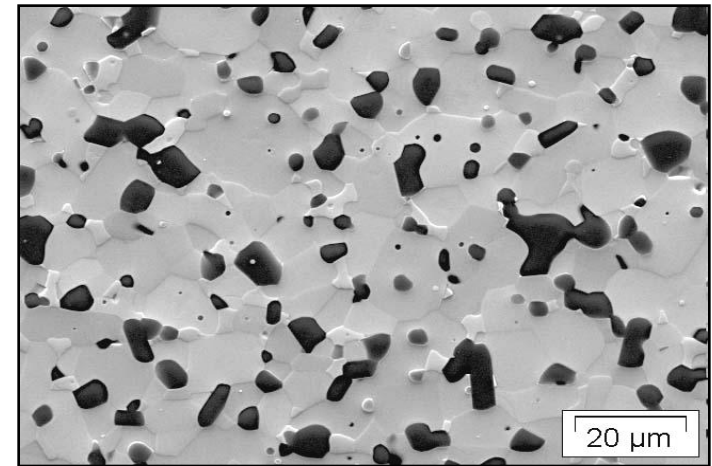
- Shuttle RCC leading edge:  $T \sim 1650^\circ\text{C}$
- Sharp leading edged vehicles:  $T > 2000^\circ\text{C}$

## ***UHTC advantages for sharp leading edges***

- Reasonable mechanical properties
- Oxidation resistance
- High thermal conductivity
  - Effective thermal radiation
  - Thermal shock resistance



Leading edges of hypersonic vehicle

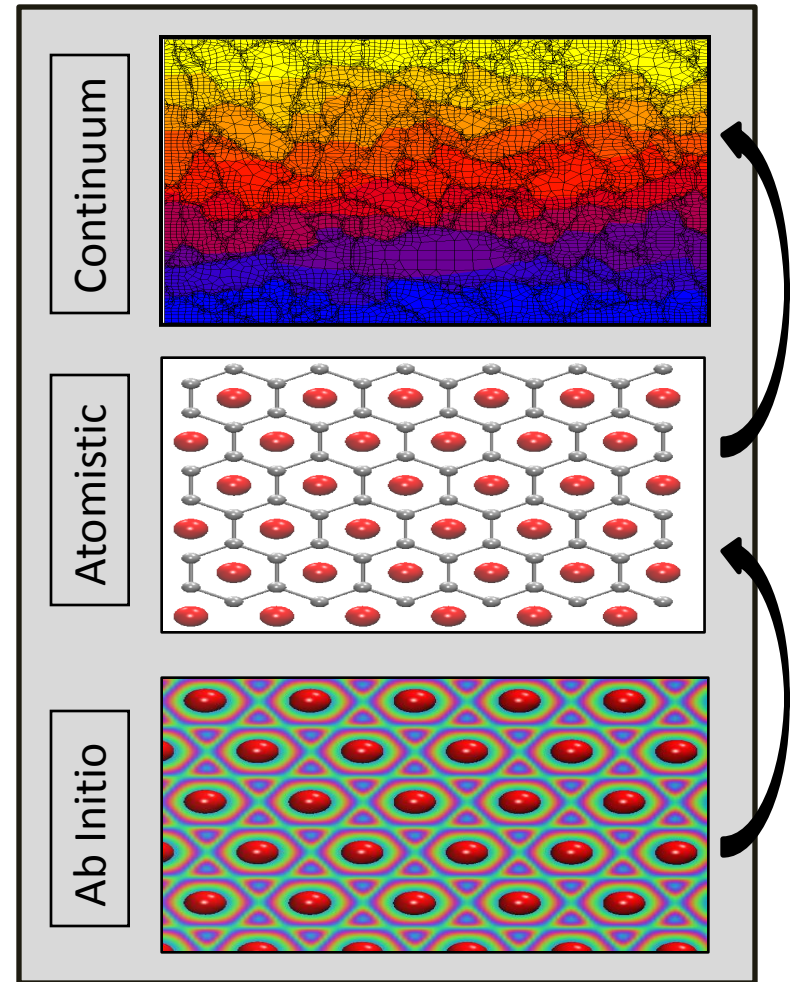


SEM image of UHTC microstructure



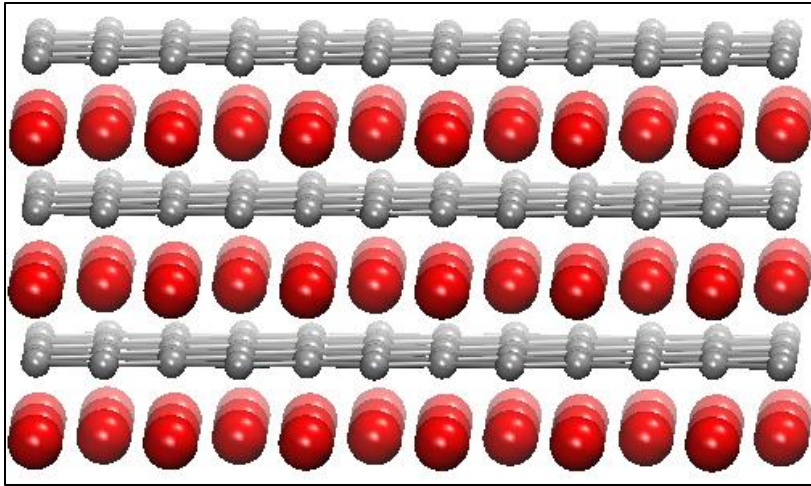
# Multiscale Modeling of UHTC

- **Materials modeling will:**
  - Discover fundamental mechanisms
  - Structure-property relationships
  - Design new materials
  - Accelerate material development
- **Framework integrates three methods:**
  - *Ab initio* – fundamental chemistry
  - *Atomistic* – thermal/mechanical
  - *Continuum* – macro properties
- **This talk focuses on thermal conductivity**
  - Atomic structure and bonding
  - Interatomic potential development
  - Lattice thermal conductivity simulations
  - Grain boundary thermal resistance
  - Imaged based FEM of GB networks

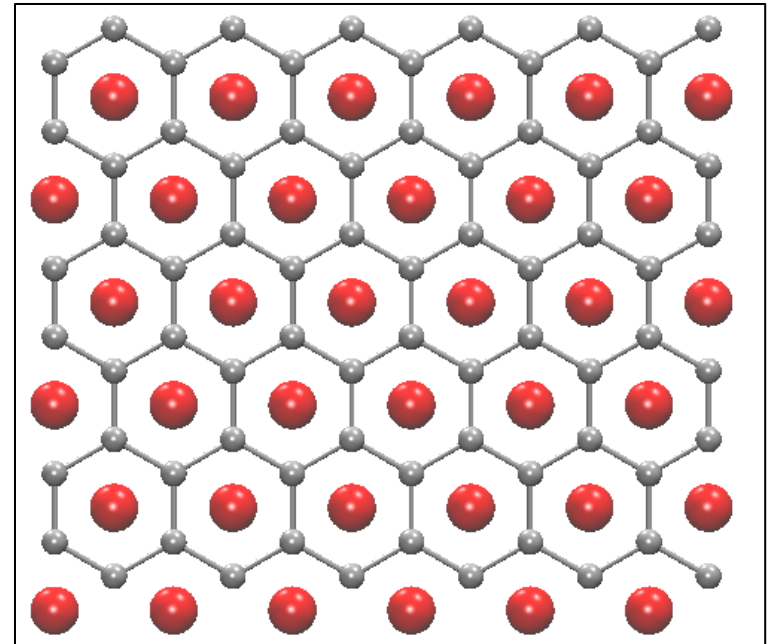




# UHTC: $\text{ZrB}_2$ and $\text{HfB}_2$



Alternating layers of  
Zr/Hf (**red**) and Boron (gray)

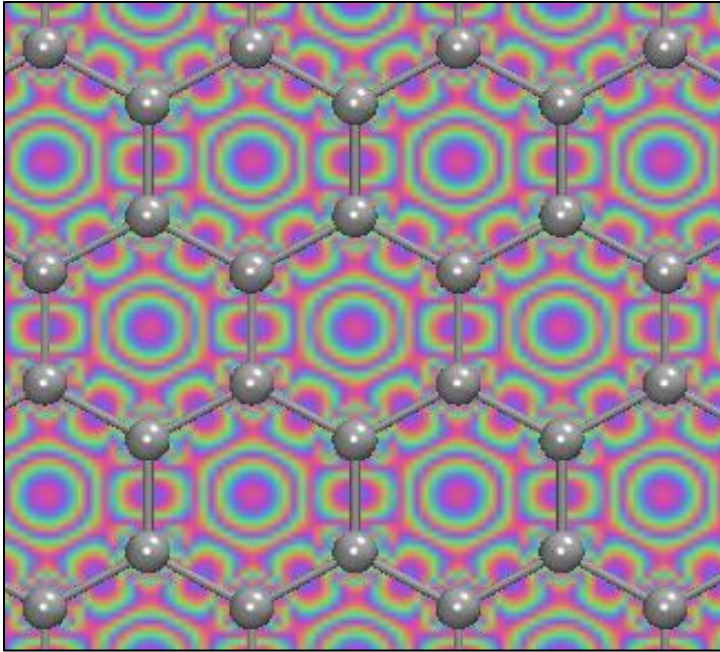


Graphitic Boron layers  
with Zr/Hf over each ring

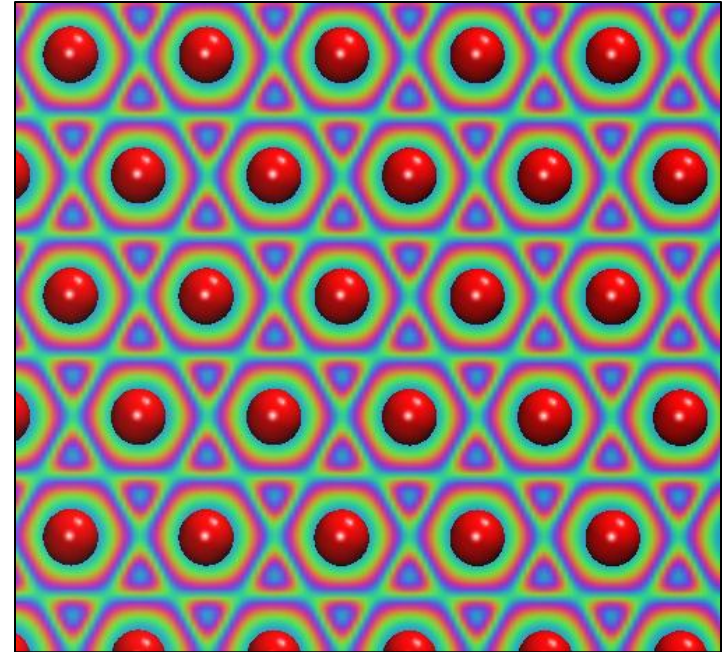




# Electron Localization Function (ELF)



Covalent bonding in Boron plane



Metallic bonding in Zr planes

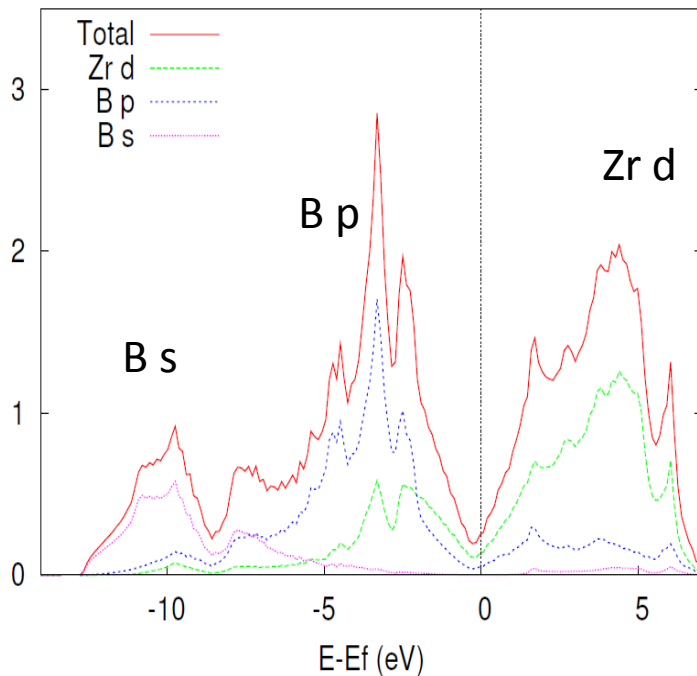
Ionic bonding between Interlayers

Blue = High  
Red = Low



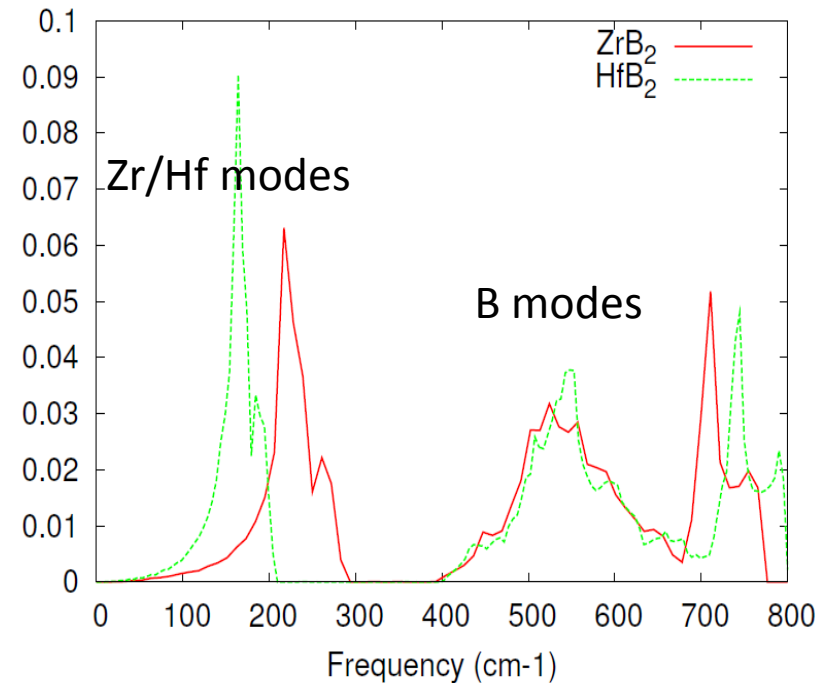
# Fundamental Properties: $\text{ZrB}_2$ & $\text{HfB}_2$

## Electronic Spectra



Electronic properties  
essentially identical

## Vibrational Spectra



Vibrational differences due  
to Zr/Hf mass difference



# Tersoff Bond Order Potential

- Two body terms ( $A, \lambda, B, \mu$ ) energy

$$E = \sum_{i \neq j} [f_R^{[ij]}(d_{ij}) + b_{ij} f_A^{[ij]}(d_{ij})]$$

$$f_R^{[ij]}(d) = A_{ij} \exp(-\lambda_{ij} d)$$

$$f_A^{[ij]}(d) = -B_{ij} \exp(-\mu_{ij} d)$$

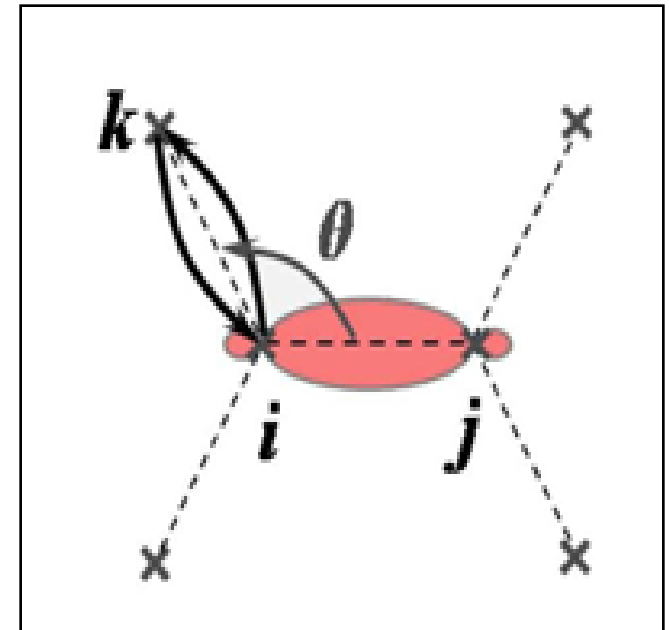
- Bond order ( $\beta, \lambda_3, n, m$ )

$$b_{ij} = (1 + \beta_i^{n_i} \zeta_{ij}^{n_i})^{-1/2n_i}$$

$$\zeta_{ij} = \sum_{k \neq i, j} f_C^{[ij]}(r_{ik}) \gamma_{ijk} g_i(\theta_{ijk}) \exp[\lambda_{3i} (d_{ij} - d_{ik})^{m_i}]$$

- Angular function ( $c, d, h$ )

$$g_i(\theta) = 1 + c_i^2 / d_i^2 - c_i^2 / [d_i^2 + (h_i - \cos \theta)^2]$$



Interatomic Energy





# Lattice Thermal Conductivity

- Green-Kubo thermal conductivity tensor

$$\kappa_{\mu\nu} = \frac{1}{Vk_B T^2} \int_0^\infty \langle J_\mu(\tau) J_\nu(0) \rangle d\tau$$

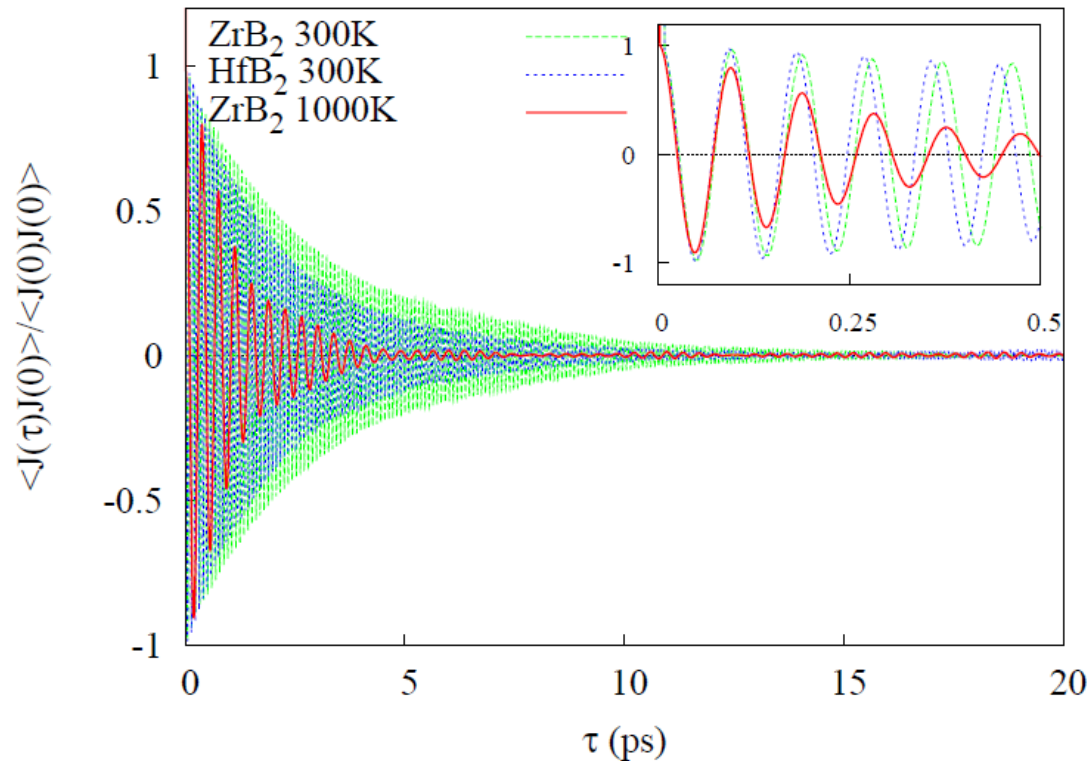
- Heat current  $J(x_i, v_i)$ , energy  $e_i$ , stress-tensor  $S_i$

$$J = \frac{1}{V} \left[ \sum_i e_i v_i - \sum_i S_i v_i \right]$$

$$J = \frac{1}{V} \left[ \sum_i e_i v_i + \frac{1}{2} \sum_{i < j} (f_{ij} \cdot (v_i + v_j)) \cdot x_{ij} \right]$$



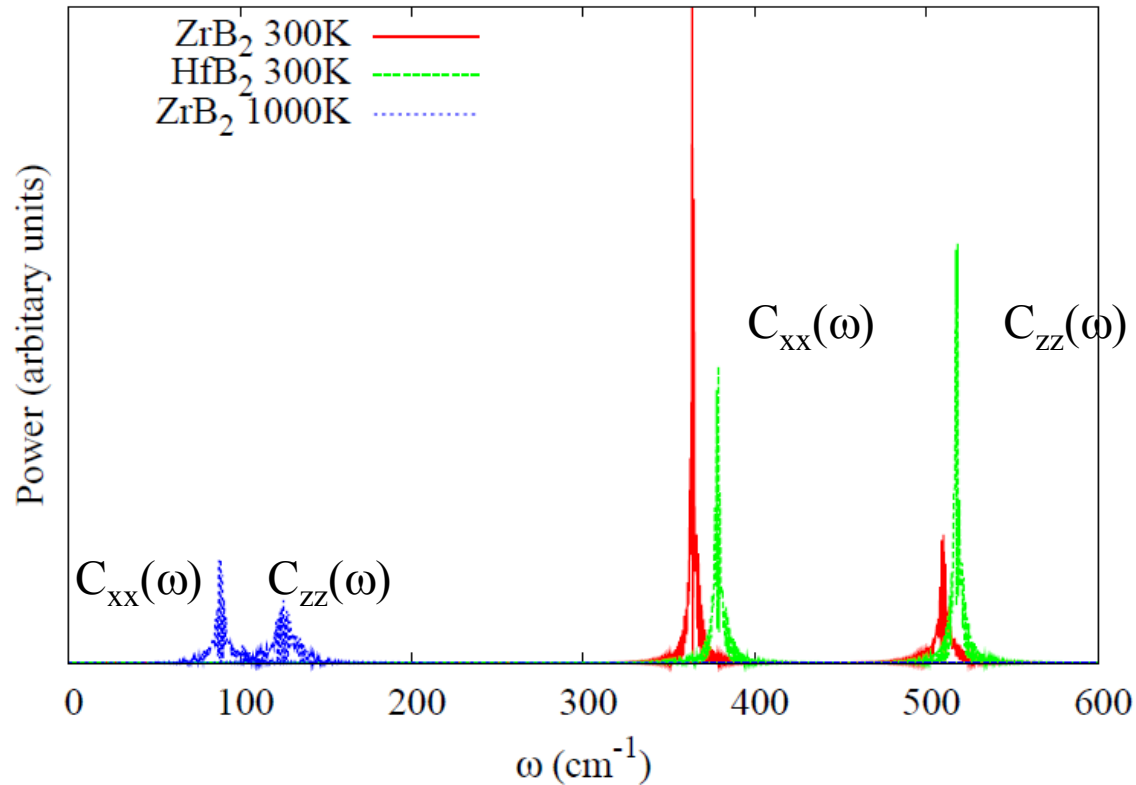
# Heat Current Correlation Function



- Monoatomic systems (e.g. Si) have monoatomic decay
- ZrB<sub>2</sub> has longer period than HfB<sub>2</sub> at T=300K
- ZrB<sub>2</sub> at T=1000K has longer period than T=300K



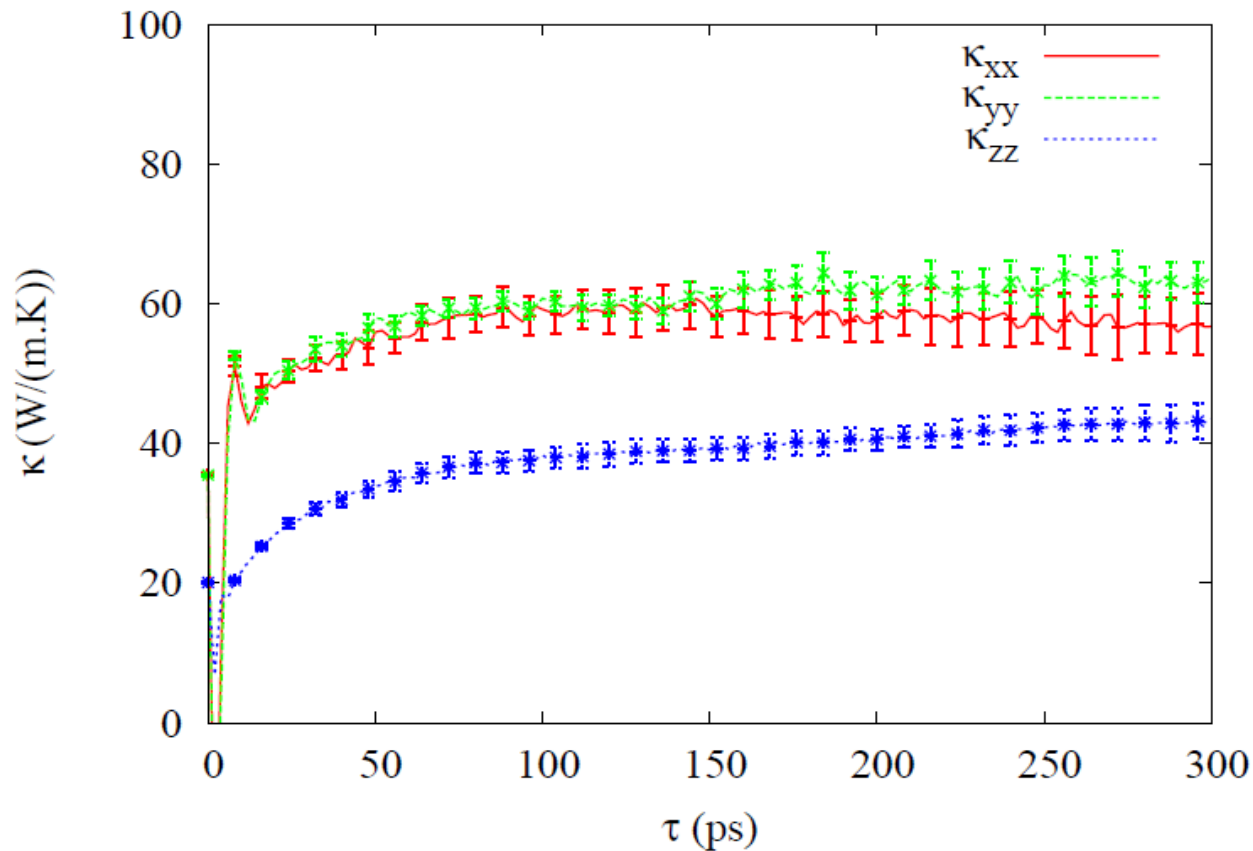
# Correlation Function Power Spectra



- Correlations oscillates with metal-B optical modes
- $C_{xx}$  and  $C_{yy}$  oscillate with in-plane mode frequency
- $C_{zz}$  oscillates with out-of-plane mode frequency



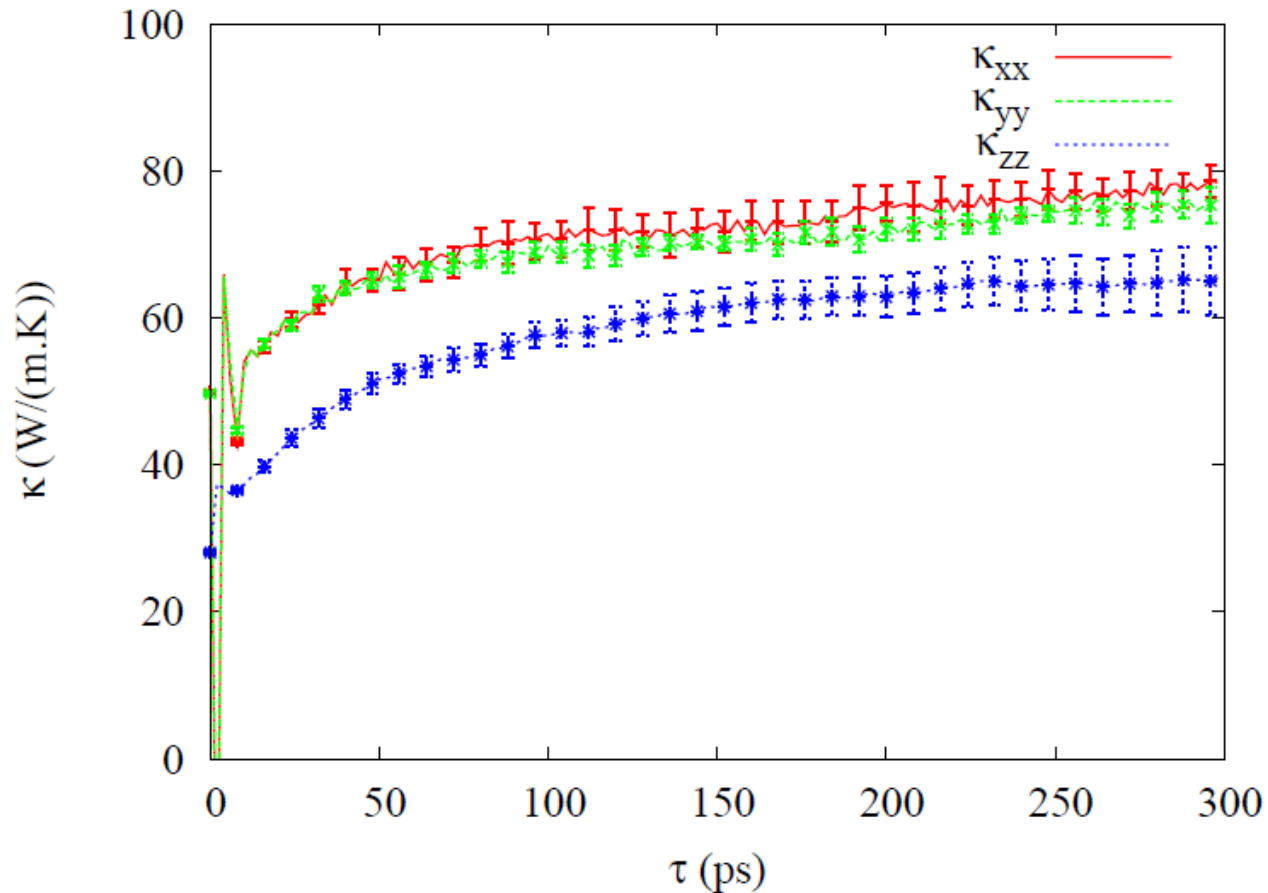
# Lattice Thermal Conductivity: $\text{ZrB}_2$



- 8 independent, 10 ns simulations,  **$T=300\text{K}$**
- 8x8x16 unit cell, 12,255 atoms
- **$\kappa_{xx}=60 \text{ W/(m.K)}$ ,  $\kappa_{zz}=40 \text{ W/(m.K)}$**



# Lattice Thermal Conductivity: HfB<sub>2</sub>

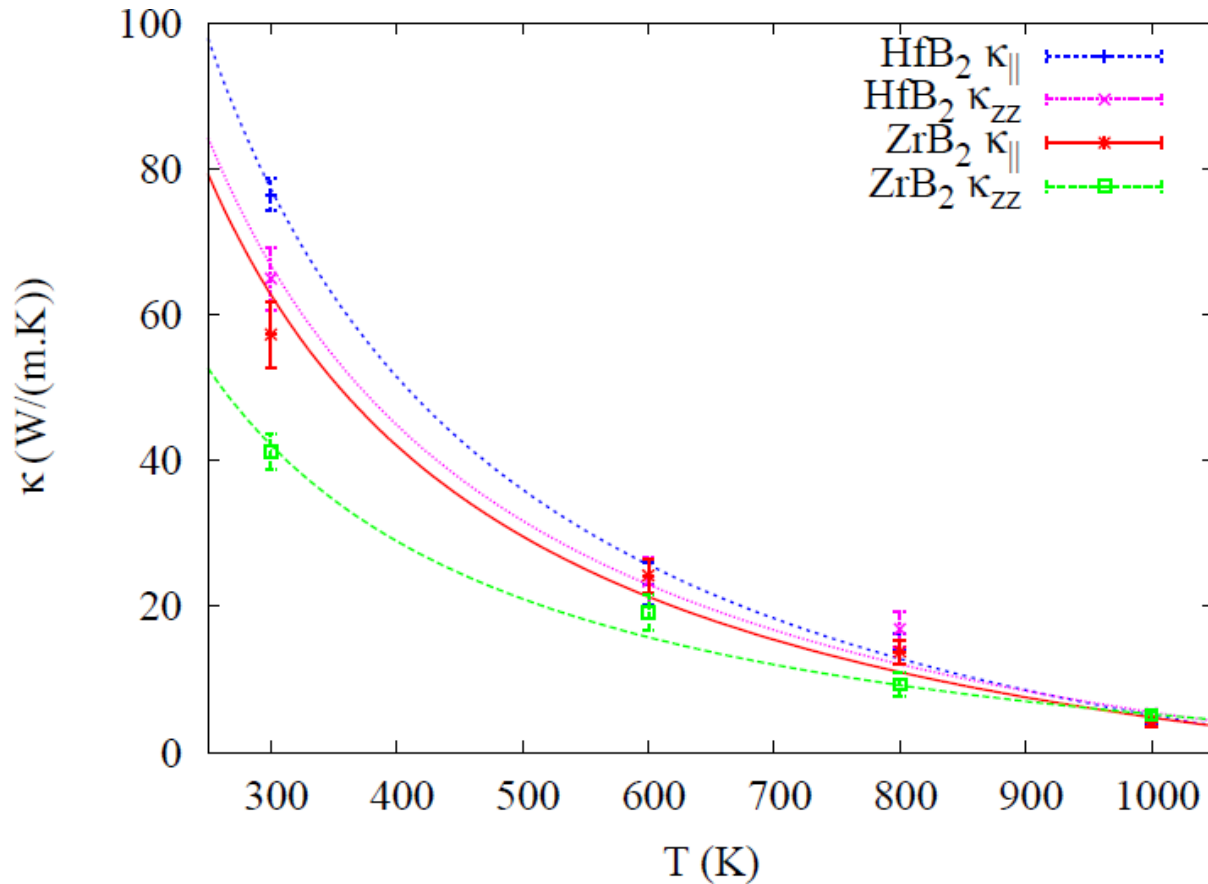


- 8 independent, 10 ns simulations
- 8x8x16 unit cell (12 atoms)= 12,255 atoms
- $\kappa_{xx}=76 \text{ W}/(\text{m}\cdot\text{K})$ ,  $\kappa_{zz}=65 \text{ W}/(\text{m}\cdot\text{K})$





# Thermal Conductivity vs Temperature



- 8 independent, 10 ns simulations for each point
- Data fit to  $1/T$  curves



# Single Crystal $\text{ZrB}_2$ Data

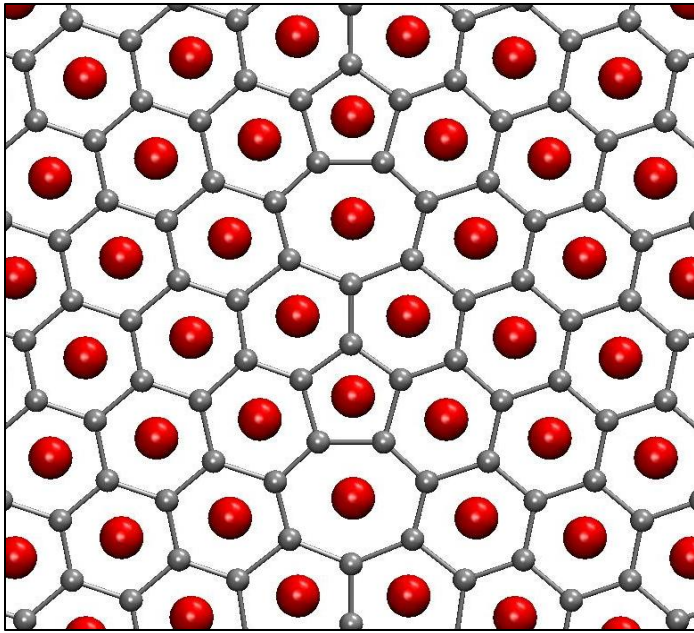
- Electron & lattice thermal conductivity

$$K = K_e + K_{lat}$$

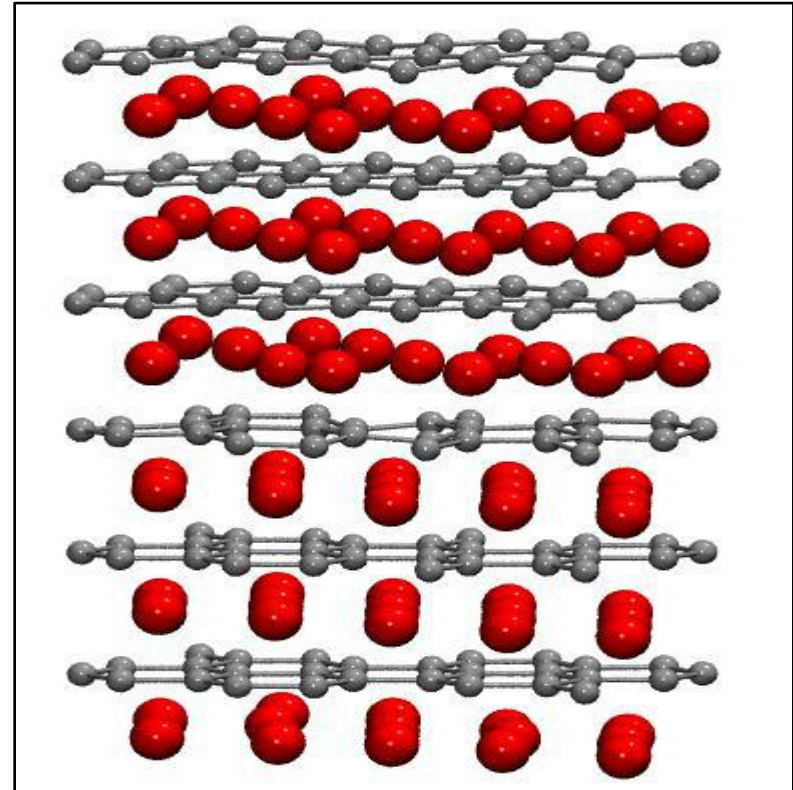
- $\kappa_{lat}$  is  $0.3\kappa$  from polycrystalline data
- Single crystal data
  - $\kappa_{xx} = 140 \text{ W/mK}$ ,  $\kappa_{zz} = 100 \text{ W/mK}$
  - 1 sample, 1 measurement
  - Defects uncharacterized
  - $\kappa_{xx} = 45 \text{ W/mK}$ ,  $\kappa_{zz} = 30 \text{ W/mK}$  (lattice)
- More data needed for  $\text{ZrB}_2$  and  $\text{HfB}_2$



# UHTC Grain Boundaries



$\Sigma 7$  symmetric tilt  
(graphene GB structure)

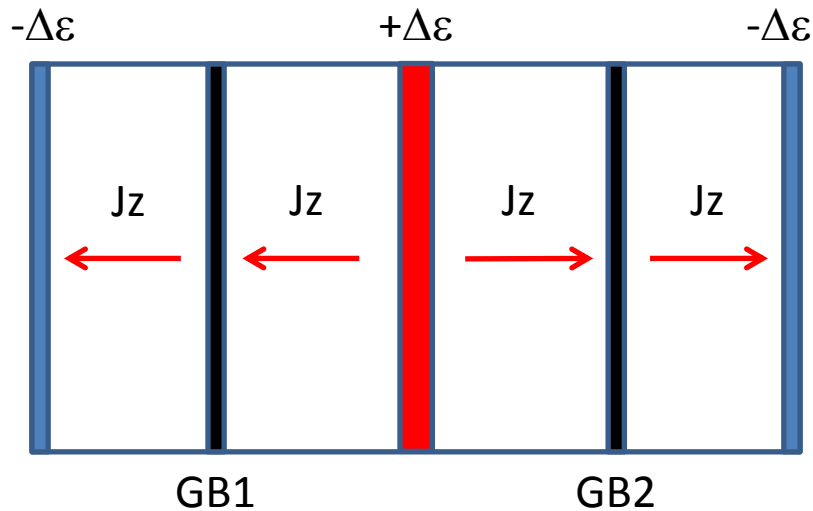


$\Sigma 7$  symmetric twist

Full *ab initio*/MD analysis of two *tilt* and two *twist* boundaries



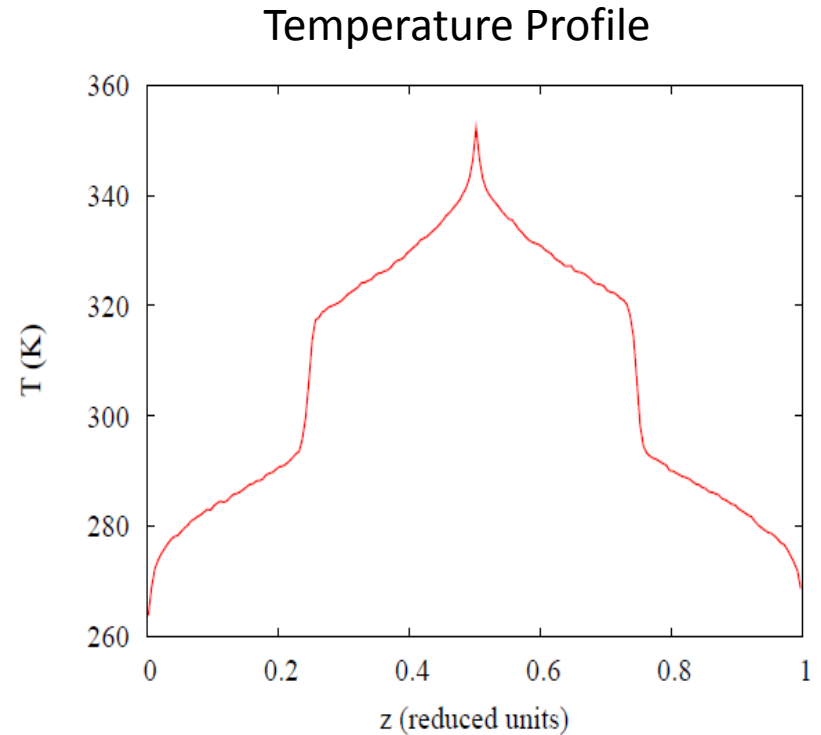
# Interface Thermal Resistance



Swap atoms to create heat source/sink

$$Q = \sigma_K \Delta T$$

$\sigma_K$  is the Kapitza conductance



GB at  $z = 0.25$  and  $0.75$



# Simulation Results

## Interface Conductance

	<i>Ab Initio</i>		DLB/Pot		
	$\gamma$ (meV/Å <sup>2</sup> )	$\Delta_z$ (Å)	$\gamma$ (meV/Å <sup>2</sup> )	$\Delta_z$ (Å)	$\sigma_K$ (GW/(m <sup>2</sup> · K))
<i>c</i> -tilt	153(369)	-	112(238)	-	1.77
<i>c</i> -twist	157(375)	0.29	111(258)	0.29	0.58
<i>a</i> -tilt	227(1040)	-	107(1380)	-	0.38/0.31
<i>a</i> -twist	212(1230)	-	118(1430)	-	0.55/0.53

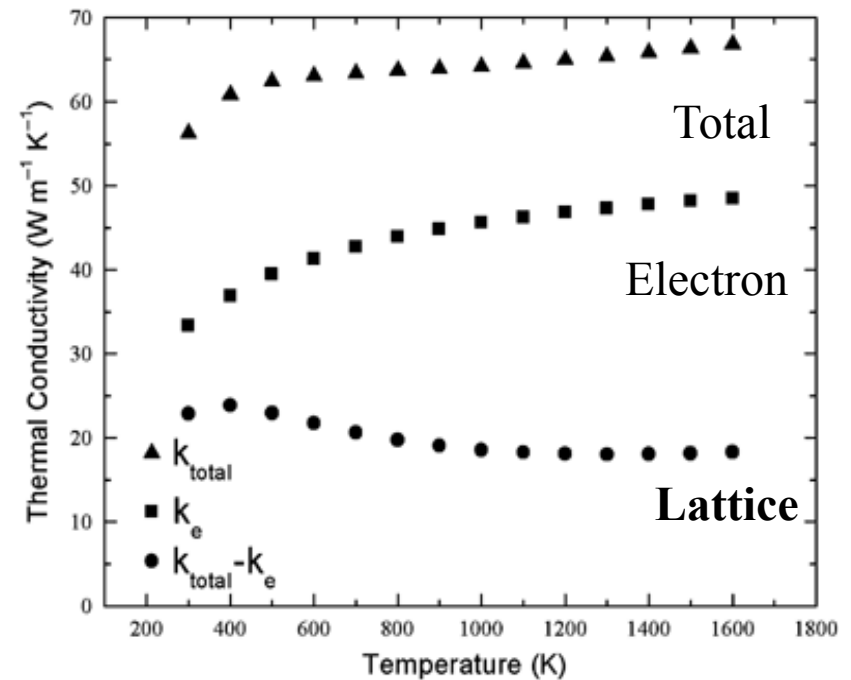
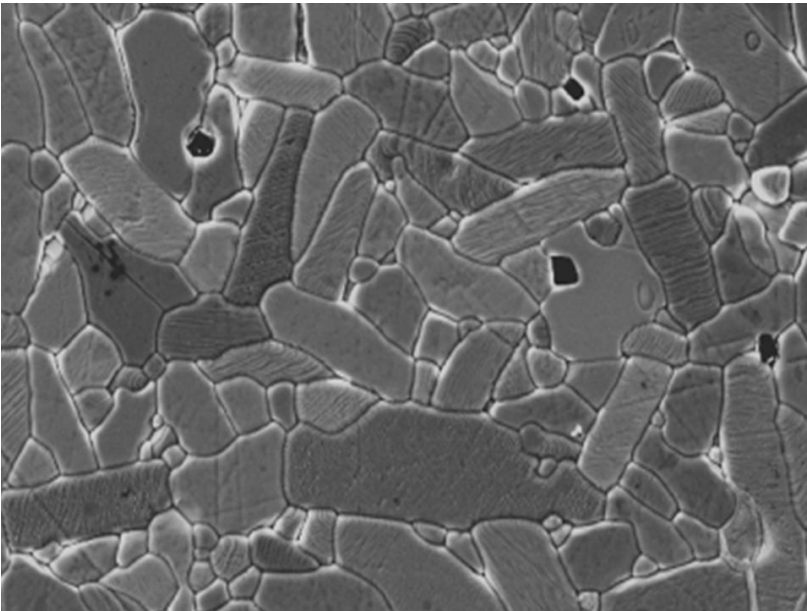
TABLE I: Energetics and thermal conductance for  $ZrB_2$  grain boundary structures from empirical potentials (DLB/Pot 1) and *ab initio*/DFT. Units for  $\gamma$  are meV/Å<sup>2</sup>,  $\Delta_z$  are Å and  $\sigma_K$  are GW/(m<sup>2</sup> · K).

- Very high thermal conductance (very low resistance)
- Experimental data indicate much lower values
- Not surprising given pristine grain boundaries
- Need: improved processing for improved GB properties
- Need: modeling more complex boundaries





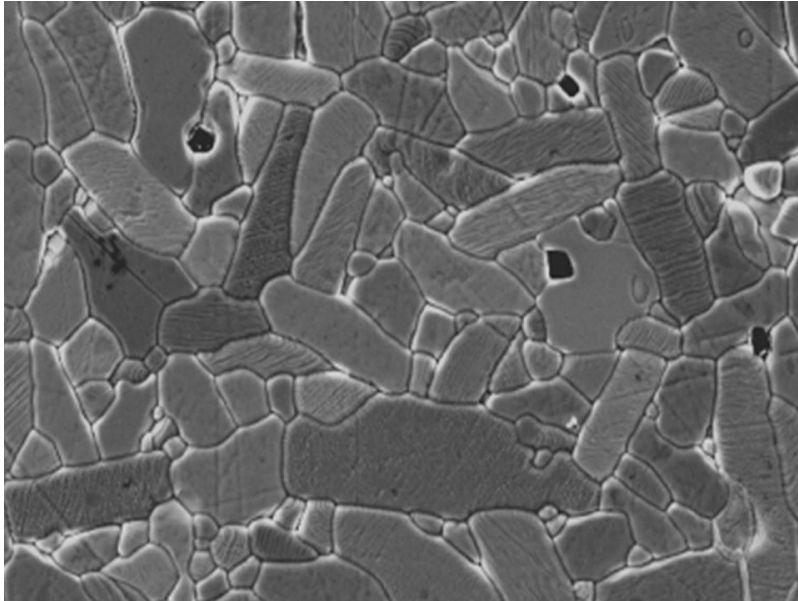
# Experimental Results: Polycrystalline $\text{ZrB}_2$



At 300K,  $\kappa_{\text{tot}} = 55 \text{ W/mK}$ ,  $\kappa_e = 33 \text{ W/mK}$ ,  $\kappa_{\text{lat}} = \underline{\underline{22 \text{ W/mK}}}$

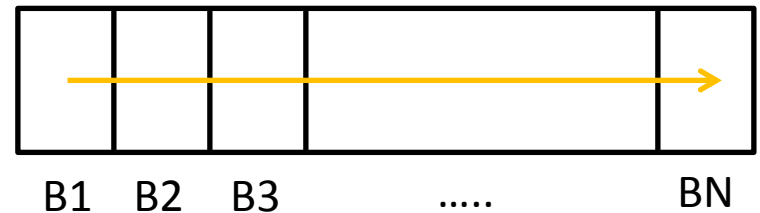


# Microstructural Model: $\text{ZrB}_2$



What is effect of grain boundary network on thermal conductivity?

Estimate with Brick Layer Model



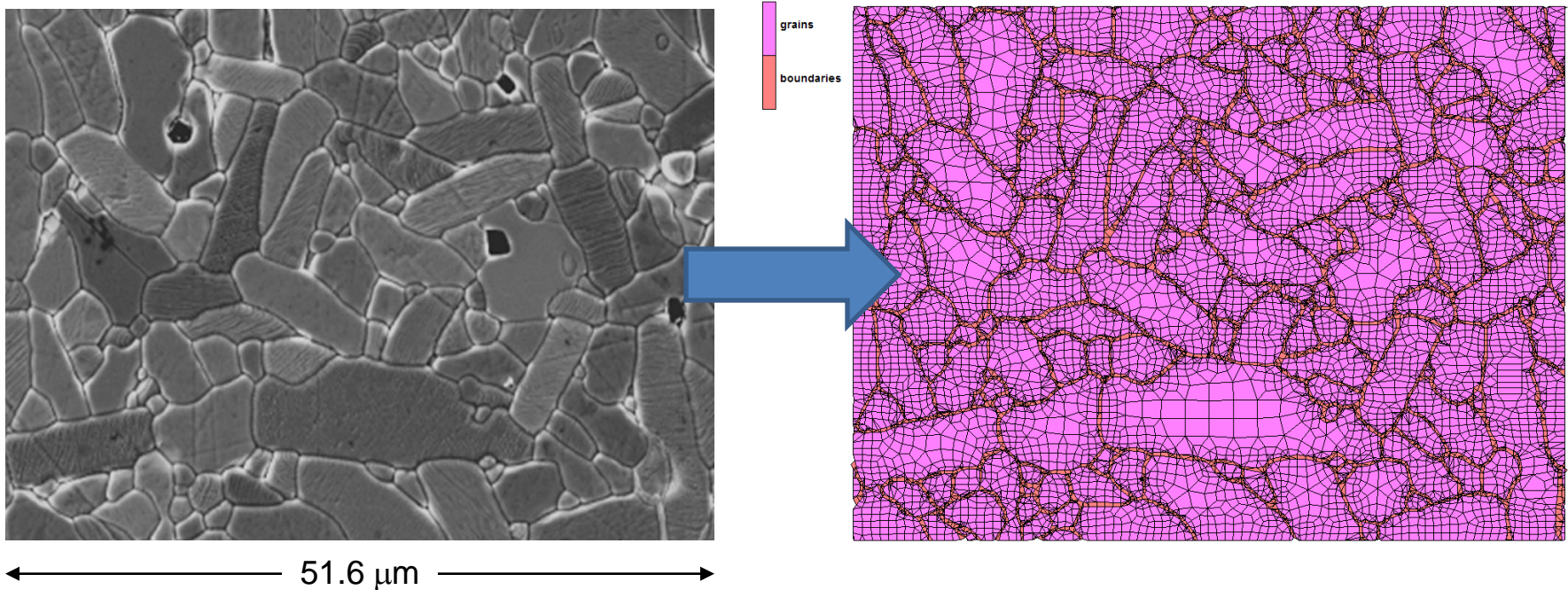
$$\frac{1}{\kappa_{eff}} = \frac{1}{\kappa_0} + \frac{R_K}{d}$$

$\kappa_{eff} = 48 \text{ W/mK}$   
using  
 $\kappa_0 = 50 \text{ W/mK}$ ,  
 $R_K = 1 \text{ m}^2\text{K/GW}$ ,  
 $d = 6\mu\text{m}$

Very small  
reduction using  
MD resistances  
and BLM!



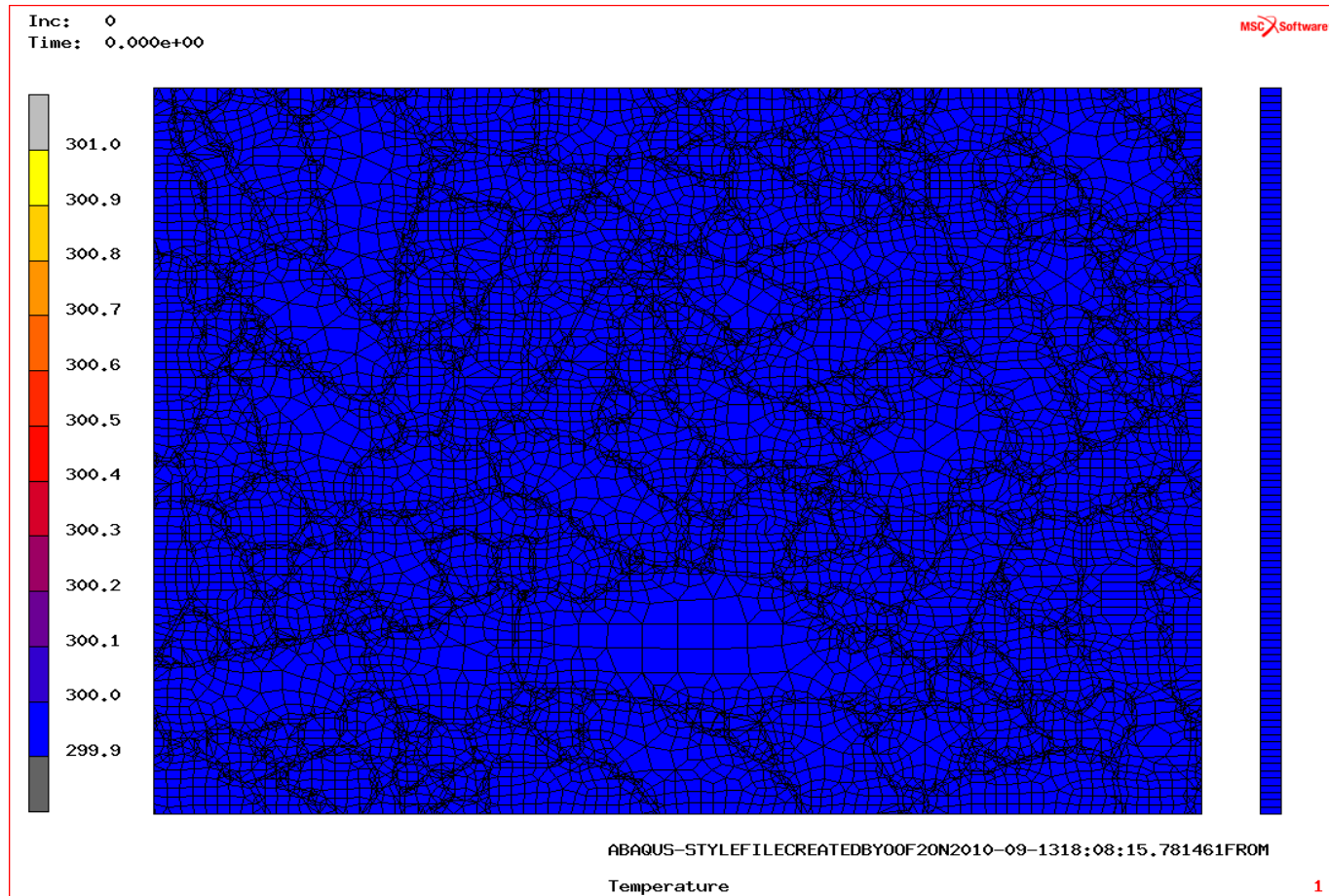
# Imaged based FEM



- Larger reduction with realistic structures and parameters?
- Realistic microstructure
- Finite element mesh from OOF2
- MD thermal conductivity for grains
- Experimental interface resistance



# Development of Steady State



Uniform thermal gradient (UTG) applied vertically across structure





# Effective Thermal Conductivity

- Boundary conditions
  - Uniform temperature gradient (UGT)
  - Uniform heat flux (UHF)
- Transport direction
  - Vertical
  - Horizontal
- Evaluate effective properties

$$\langle q \rangle = -k_{eff} \cdot \langle \nabla T \rangle$$

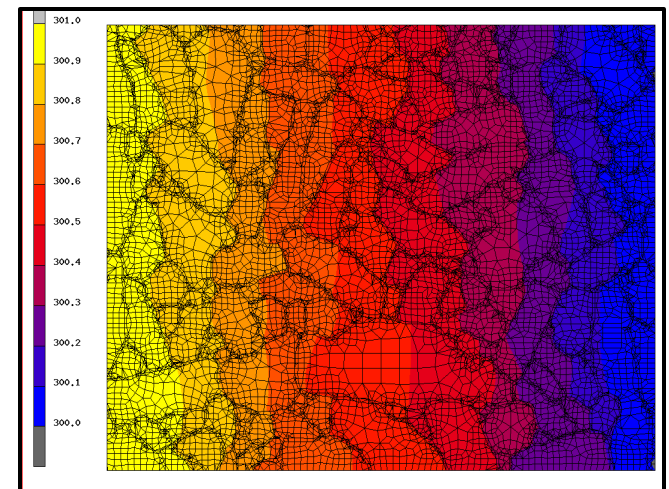
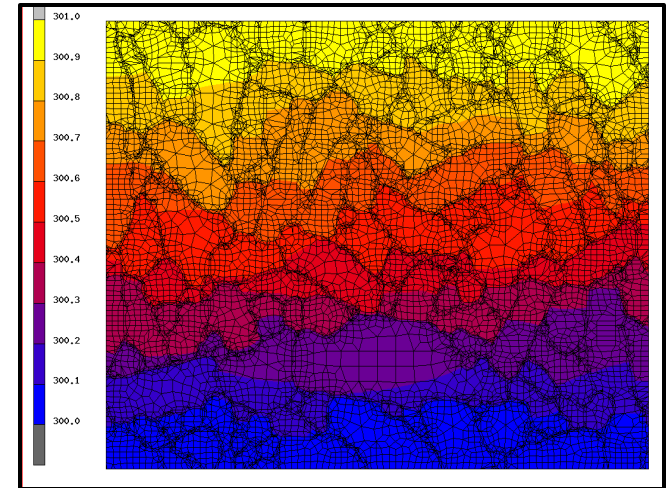
$k_{eff}$  = effective thermal conductivity

$\langle q \rangle$  = volume averaged heat flux

$\langle \nabla T \rangle$  = volume averaged temperature gradient

- Is microstructure “representative”???

$$K_{UHF} \leq K \leq K_{UTG}$$







# Effective Thermal Conductivity

BC Type	Parameter	Vertical	Horizontal
UGT	$\langle q \rangle$	-27.32	19.05
	$\langle dT/ds \rangle$	1.56	-1.17
	$\kappa_{eff}$	<b>17.48</b>	<b>16.24</b>
UHF	$\langle q \rangle$	-28.13	28.05
	$\langle dT/ds \rangle$	1.68	-1.76
	$\kappa_{eff}$	<b>16.72</b>	<b>15.93</b>

Comparison of results:

- BLM  $\kappa_{eff} = 15.4$  (series model)
- Rule of mixtures  $\kappa_{eff} = 44.14$  (parallel model)
- FEM has series and parallel contributions
- BLM has very good agreement with FEM



# Conclusions

- **NASA ARC computational materials modeling:**
  - Ablative composites
  - Ultra high temperature ceramics
- **Multiscale framework for UHTC:**
  - *Ab Initio* – bonding, electronic & vibrational spectra
  - Atomistic simulation – bulk and interfacial thermal conductivity
  - Continuum – microstructural modeling and effective properties
  - Iteration with experiment needed to “close” loop
- **Modeling unanswered questions:**
  - Interatomic potential fidelity
  - Complex grain boundary structural models and properties
- **Experimental unanswered questions:**
  - Single crystal thermal conductivity
  - Electronic vs lattice carrier breakdown
  - Grain boundary atomic structures and properties
  - Improved grain boundaries from improved processing